5-4-2018

Phonon Dynamics of Alkali Metals in the HCP Lattice Structure

Jake Christensen
Utah State University

Phonon Dynamics of Alkali Metals in the HCP Lattice Structure

Jake Christensen

May 4, 2018

Abstract

An Embedded-Atom-Method model that is successful at describing the vibrational properties of alkali metals in the BCC crystal structure is applied to the HCP structure. Phonon dispersion curves, density of states, and Debye temperatures are calculalated for Li, Na, K, Rb, and Cs. Comparison of BCC, FCC and HCP Debye temperatures show that BCC is the preferred structure at higher temperatures, which agrees with experiment.

1 Introduction

Embedded-atom-method (EAM) models have been used to study many material properties of FCC and BCC metals, and have been successful at describing vibrational dynamics [1]. In 2012 Wilson and Riffe constructed an EAM model that predicts phonon dispersion and Debye temperatures in excellent agreement with experimental data for the alkali metals [2]. Although Wilson did some separate calculations on FCC metals, the model was primarily used for BCC alkalis [3].

It is well known that lithium and sodium undergo a phase transition to a close-packed structure at low temperature [4, 5]. Thus, studying the behaviour of the alkali metals in a close packed structure can reveal useful information about the Wilson-Riffe model. Also, because of the success of the Wilson-Riffe model, there is reason to believe that it will model close-packed structures accurately. Here, we explore the alkali metals in a hexagonal close-packed (HCP) structure. Dispersion curves, density of states, and Debye temperatures have been calculated and plotted.

2 The EAM Model

The EAM model is a model of the potential energy of a crystal. The model incorporates pair-wise interactions of atoms, as well as an embedding energy, which accounts for interactions of the atoms with the electron charge density of the lattice. With these two pieces, the potential energy for the ith atom in the lattice can be expressed as

$$U_i = \frac{1}{2}\sum_j \phi(r_{ij}) + F(\rho_i), \tag{1}$$

where j labels atoms in the solid, r_{ij} is the distance between the atoms i and j, ϕ is the pair potential function, F is the embedding energy function, and ρ_i is the electron density at the location of atom i. The density ρ_i can be written as a sum of individual atomic densties $f(r_{ij})$ from the atoms surrounding it,

$$\rho_i = \sum_j f(r_{ij}). \tag{2}$$

2.1 The Dynamical Matrix

To describe the dynamics of the lattice, we follow the formulation of Ibach and Luth [6] by expanding the potential energy of atom i [Eq. (1)] in a Taylor series expansion in small displacements $s_{n\alpha i}$ from equilibrium. Here, α labels atoms the basis, n labels unit cells, and i labels the Cartesian component of displacement. The Taylor expansion is

$$U(r_{n\alpha i} + s_{n\alpha i}) = U(r_{n\alpha i}) + \frac{1}{2} \sum_{m\beta j, n\alpha i} \frac{\partial^2 U}{\partial r_{n\alpha i} \partial r_{m\beta j}} s_{n\alpha i} s_{m\beta j} + ..., \tag{3}$$

where the sum runs over all atoms in all unit cells in the x, y, and z directions. By taking a harmonic approach and ignoring higher order terms, this equation represents an extension of the harmonic oscillator potential in the case of many particles. The derivatives of the potential,

$$\Phi_{n\alpha i}^{m\beta j} \equiv \frac{\partial^2 U}{\partial r_{n\alpha i} \partial r_{m\beta j}}, \tag{4}$$

have dimensions of spring constants and are called the coupling constants. These take the role of spring constants in the equation of motion for the i component of atom $n\alpha$,

$$M_\alpha \ddot{s}_{n\alpha i} + \sum_{m\beta j} \Phi_{n\alpha i}^{m\beta j} = 0. \tag{5}$$

Here M_α is the mass of atom α. This gives rise to $3rN$ differectial equations from the N unit cells each with r atoms. However, with periodic structures, significant simplifications can be achieved by using a suitable ansatz. We write the displacements $s_{n\alpha i}$ as a plane wave that is only defined at the atom locations $r_{n\alpha}$,

$$s_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}, \tag{6}$$

Here u is the amplitude of a given wave with wave vector $\mathbf{q}$, and ω is the associated frequency. Substituting (6) into (5) and performing some simplifications gives us the dynamical matrix, whose eigenvalues tell us the frequency squared of the vibrations, and the associated eigenvectors give us the polarizations. The elements of the dynamical matrix take the form

$$D_{\alpha i}^{\beta j} = \sum_m \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{iq(r_m - r_n)}. \tag{7}$$

Diagonalizing the dynamical matrix for a series of wave vectors along various high-symmetry directions gives us dispersion curves, like those shown in Fig. 1 for BCC lithium.

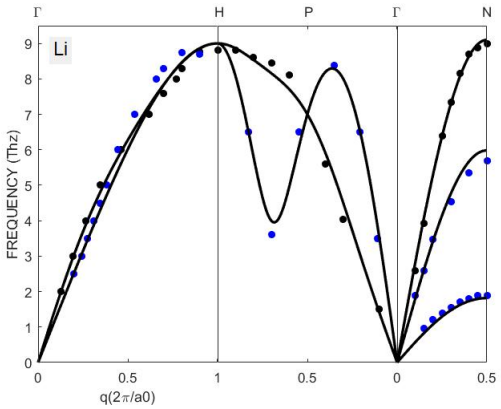

Figure 1: Lithium BCC Dispersion Curves

2.2 Wilson-Riffe EAM Model

In the Wilson-Riffe EAM model, previously introduced forms of the pair potential, embedding energy, and atomic density are used. The pair potential model is taken from Wang and Boerker [7]

$$\phi(r) = \sum_{n=0}^{6} K_n \left(\frac{r}{r_1} - 1 \right)^n exp\left(- n\alpha (\frac{r}{r_1} - 1)^2 \right), \tag{8}$$

and the embedding energy and atomic density are taken from Johnson and Oh [8],

$$F(\rho) = -(E_{coh} - E_{1v}^{UF}) \left[1 - \lambda \ln(\frac{\rho}{\rho_e}) \right] \left(\frac{\rho}{\rho_e} \right)^{\lambda} \tag{9}$$

and

$$f(r) = f_1 \exp\left(- \beta (\frac{r}{r_1} - 1) \right). \tag{10}$$

Using this model to derive our dynamical matrix, and evaluating the matrix at certain wave vectors, allows us to express the values of K_n in terms of experimental data. λ, α, and β are left as adjustable parameters. The combination of experimental inputs and free parameters allows the Wilson-Riffe model to produce highly accurate results for phonon dispersion curves of the alkalis in the BCC structure.

3 Code Development

In order to apply the Wilson-Riffe model to alkali metals in HCP structures several changes had to be made to the code. When I began the project, the code was only able to perform calculations for crystal structures with one atom per unit cell. The one atom per unit cell scenario allows several simplifications to be made in calculating the dynamical matrix, and it was these simplifications that were coded in. However, for structures with more atoms per unit cell, no general simplifications can be made. Thus, I came up with a new scheme to efficiently calculate vibrational properties for an arbitrary lattice structure with an arbitrary number of atoms per unit cell.

The scheme is very straightforward. The biggest computational hurdle is calculating the dynamical matrix many times, once for each wave vector you wish to analyze. In order to streamline this I simply inserted a step in which the coupling constants $\Phi_{n\alpha i}^{m\beta j}$ are calculated once and stored in a file, and then read into memory during computation time. With this, the work required to calculate an element of the dynamical matrix is $O(N)$, where N is the number of atoms being considered. This is a vast improvement from the $O(N^2)$ work required if one were to calculate the coupling constants for each wave vector to be analyzed.

3.1 Dispersion Curves

With the appropriate algorithms developed, dispersion curves for HCP alkali metals were able to be calculated. Since the HCP structure has 2 atoms per unit cell, the dispersion curves have 6 branches in any direction. The dispersion curves for Li, Na, K, Rb, and Cs are shown in Fig. 2 below.

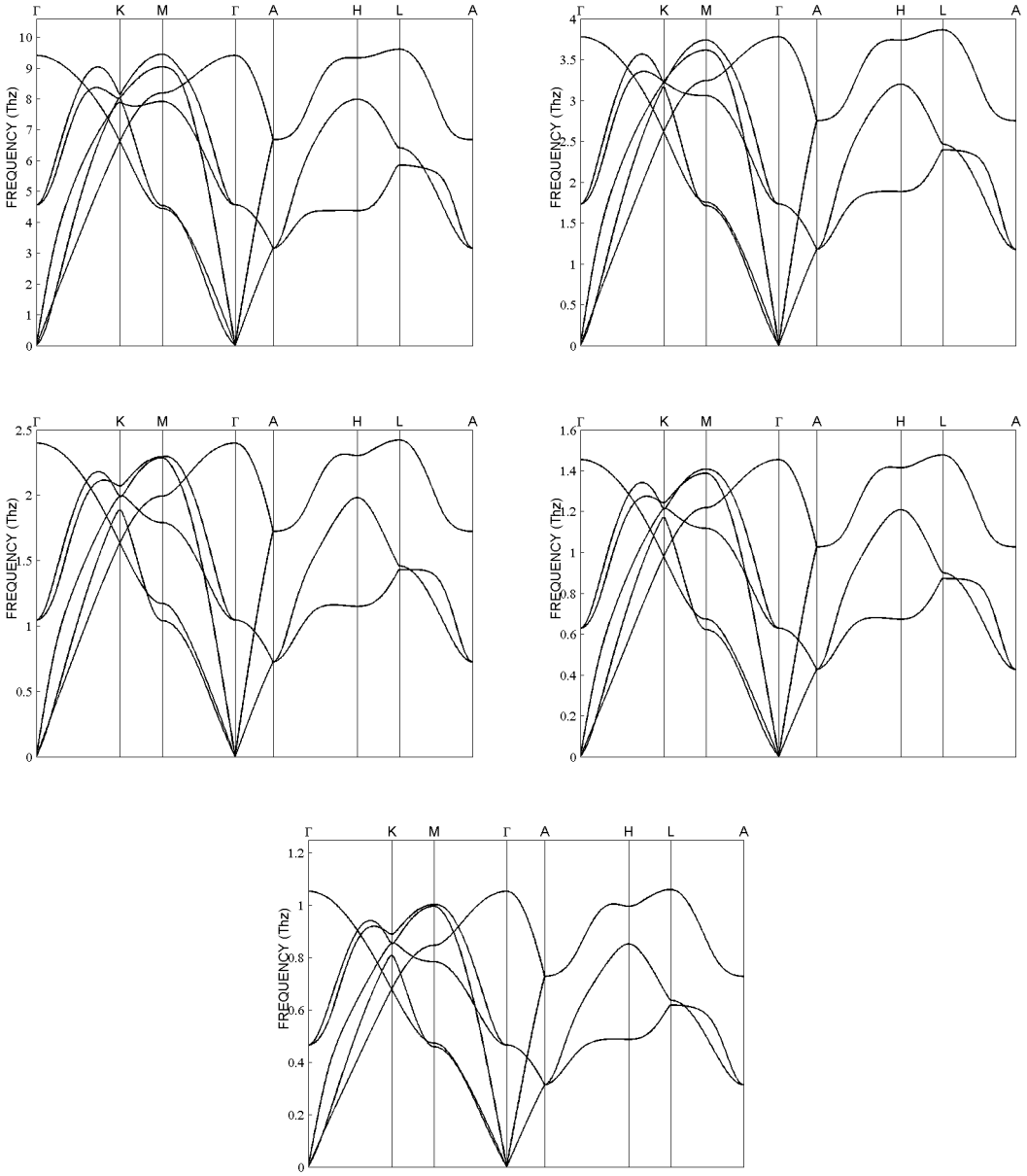

Figure 2: (In order of top-left, top-right, middle left, etc.) Dispersion Curves for HCP Li, Na, K, Rb, and Cs.

3.2 Density of States

The Density of States (DOS) is an incredibly useful function to calculate when working out thermal and vibrational properties of crystal structures. From the DOS one can work out Debye temperatures, which in turn can be used to calculate specific heat, thermal expansion coefficients, entropy, and more.

The DOS measures how many available modes are in some small width of frequency. To calculate this, one must create a mesh of k-space points in the first brillouin zone of the lattice and solve the dynamical matrix at each point. The first brillouin zone for the HCP lattice is a fairly simple hexaganol

zone, shown in Fig. 3 below.

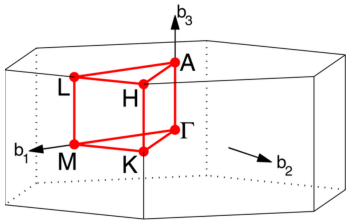

Figure 3: First Brillouin zone of the HCP lattice

From these solved frequencies, one can create a histogram of frequencies which is used as the DOS. Thus, creating as fine a mesh as possible is essential. For our calculations, we used on the order of 10^6 k-space points.

Using the same scheme to calculate the dynamical matrix that was used for the dispersion curves, we generated DOSs for Li, Na, K, Rb, and Cs, and these results are shown in Fig. 4 and Fig. 5 below.

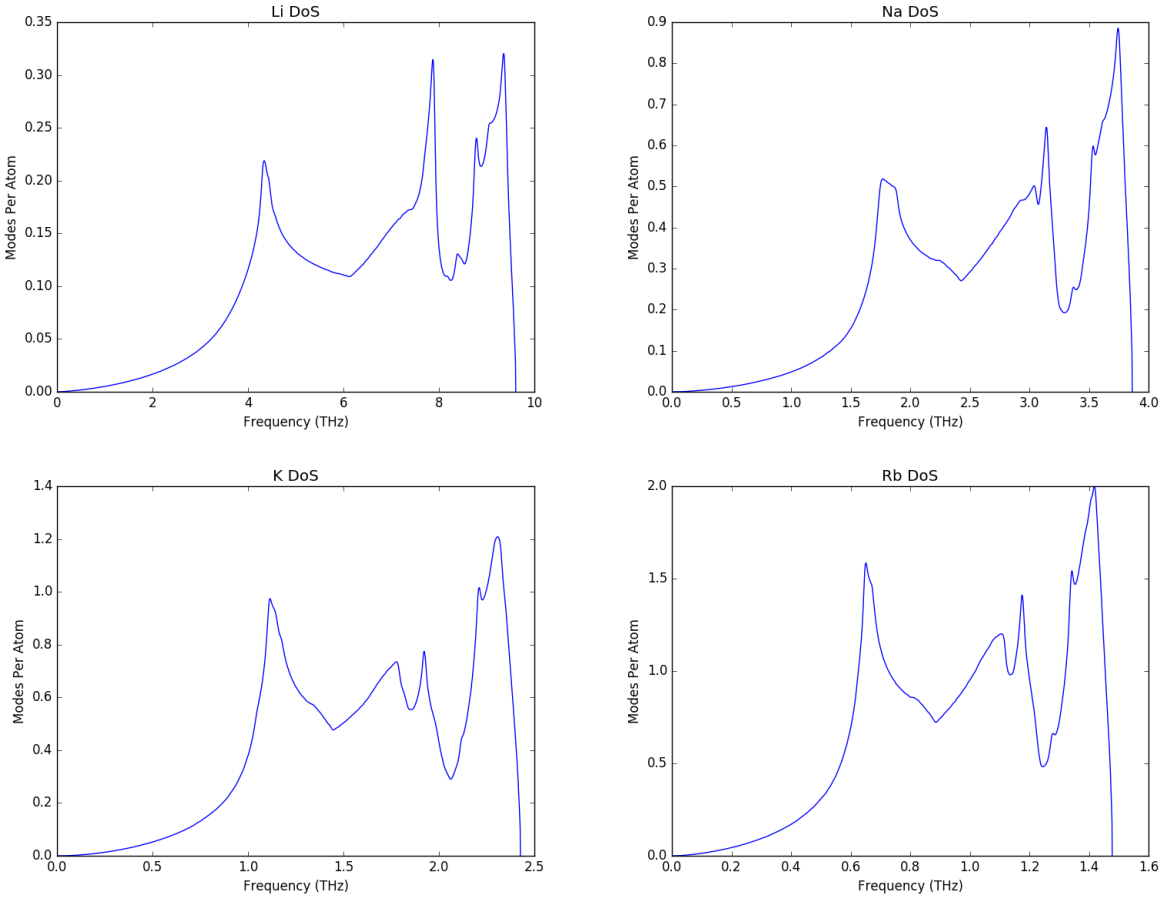

Figure 4: Density of states for HCP Li, Na, K, and Rb.

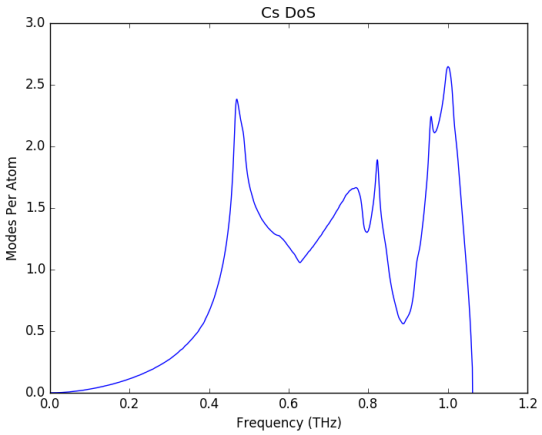

Figure 5: Density of states for Cs.

3.3 Debye Temperatures

With an accurate density of states, denoted be $g(\omega)$ below, the Debye temperatures $\Theta_D(n)$ can be calculated,

$$\Theta_D(n) = \frac{\hbar}{k_B}\left(\frac{n+3}{n}\frac{\int \omega^n g(\omega)d\omega}{\int g(\omega)d\omega}\right)^{\frac{1}{n}}. \tag{11}$$

This is a straightforward calculation, and the results for each of the alkalis are shown below in Fig. 6, Fig. 7, and Fig. 8, each compared with their BCC and FCC values.

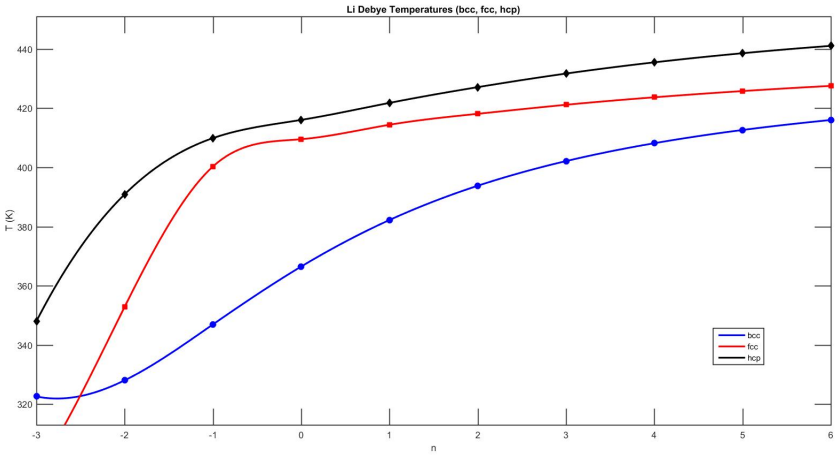

Figure 6: Debye temperatures for Li in HCP, BCC and FCC structures.

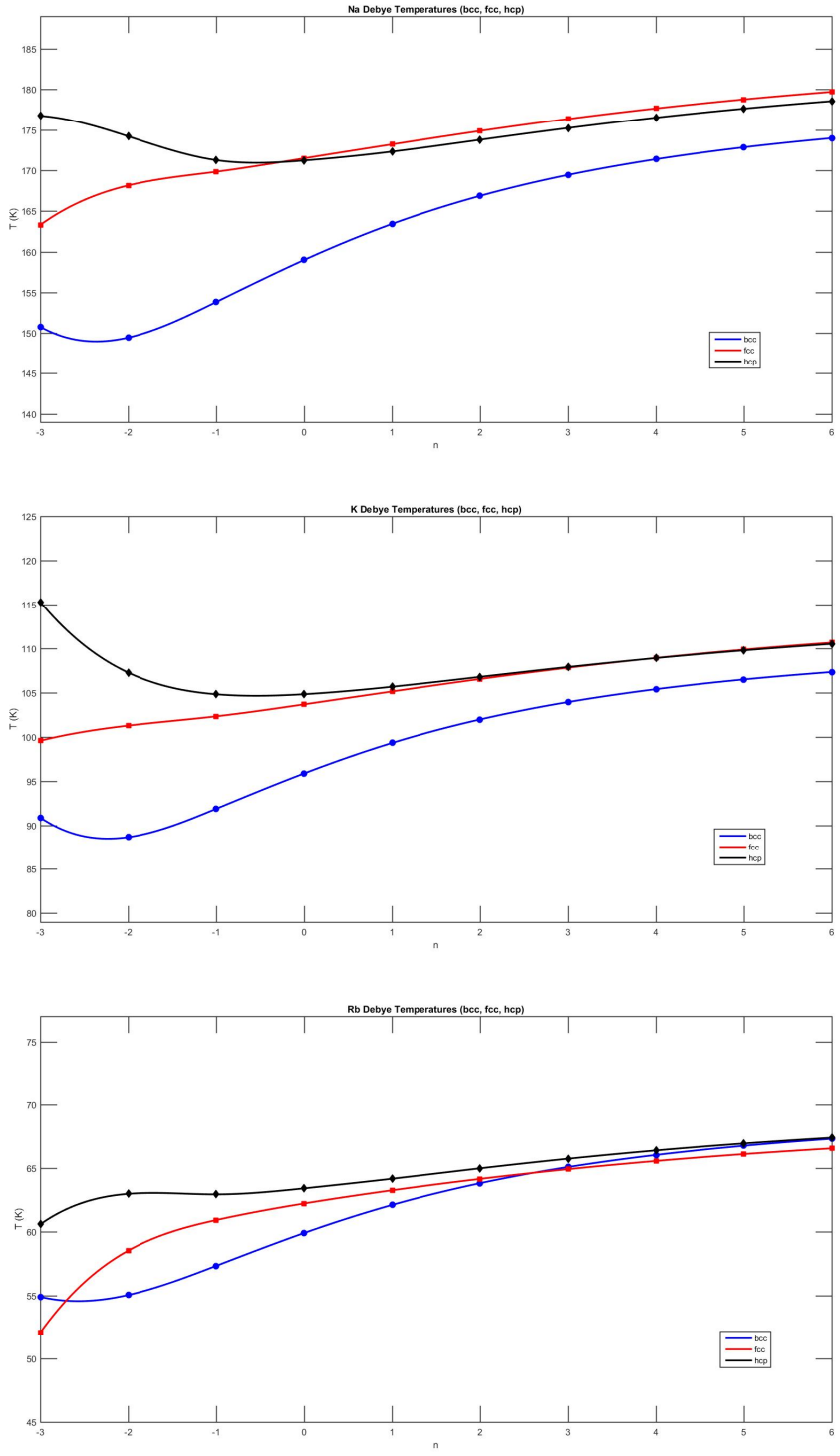

Figure 7: Debye temperatures for Na, K, and Rb in HCP, BCC and FCC structures.

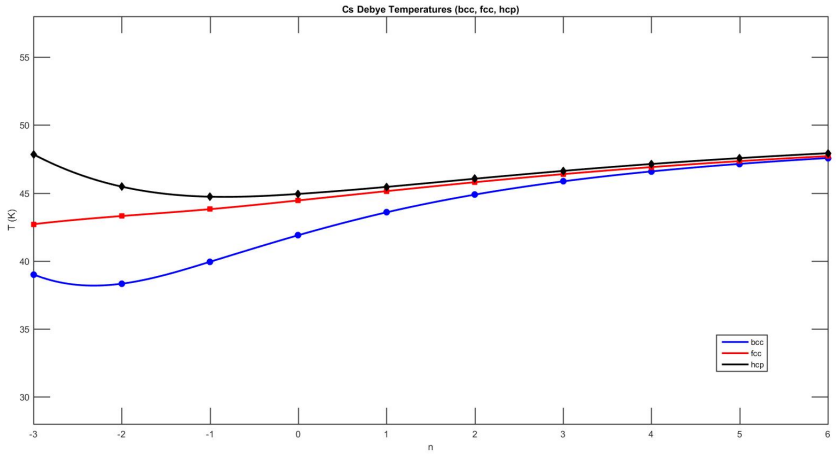

Figure 8: Debye temperatures for Cs in HCP, BCC and FCC structures.

Notice that the BCC metals tend to have lower Debye temperatures. This explains why BCC is the prefered structure: lower Debye temperatures indicate higher entropy and thus lower free energy at higher temperatures.

4 Conclusion

The Wilson-Rifffe model shed some interesting light onto the vibrational properties of close-packed structures. The Debye temperatures of lithium and sodium suggest that BCC is the prefered structure at higher temperatures, which is consistent with experiment. Further investigation into close-packed structures will reveal even more. Moving forward, we plan to apply the model to the 9R structure, as well as performing surface calculations for FCC, HCP and 9R.

References

[1] M. S. Daw, S. M. Folles, and M. I. Baskes, Material Science Reports **9**, 251 (1993)
[2] R. B. Wilson and D. M. Riffe, Condensed Matter **24**, 335401 (2012)
[3] R. B. Wilson, *An embedded atom method investigation into the lattice dynamics of metallic surfaces* (2011)
[4] A. H. Daane, R. E. Rundle, H. G. Smith, and F. H. Spedding, Acta Cryst. **7**, 532 (1954)
[5] C. S. Barret, Acta Cryst. **9**, 671 (1956)
[6] H. Ibach and H. Luth, *Solid State Physics* (New York, 1993)
[7] Y. R. Wang and D. B. Boerker, Journal of Applied Physics **78**, 122 (1995)
[8] R. A. Johnson and D. J. Oh, Journal of Material Research **4**, 1195 (1989)